

Lateral inhomogeneities and termination in ultrathin block copolymer films

R. Fink¹, Th. Schmidt¹, N. Rehse², G. Krausch², I. Koprinarov³, H. Ade⁴

¹Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

²Physikalische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany

³Brockhouse Institute for Materials Research, McMaster Univ., Hamilton, ON L8S 4M1, Canada

⁴North Carolina State Univ., Dept. Of Physics, Raleigh, NC 27695, USA

INTRODUCTION

Linear chain-like molecules consisting of blocks of chemically different components (so-called block-copolymers) in many cases form long-range ordered supramolecular structures. The reason for this behavior is the interplay between phase separation of the different components and the molecular unity in the single molecules. The size of the forming structures depends on the size of the molecules and ranges from about 10 to 100 nm. This is usually called “microphase separation” or “micro domain formation”. Due to the differences in the surface free energy of the polymers the structure of the micro domains of the surfaces and interfaces can be manipulated. Whereas the structure and morphology of diblock copolymers has been intensely investigated, the investigation of more complex structures (multiblock copolymers, graft polymers, star-like copolymers, etc.) has started only recently.

Recent investigations demonstrate more complex surface and thin film morphologies [1-3]. E.g., an ABC-triblock copolymer consisting of polystyrene (PS), polybutadiene (PB) and polymethylmethacrylate (PMMA), which forms lamellar-like structures in bulk, forms lateral structures at the surface, since the PB-center block (PB) has the lowest surface free energy [4]. To investigate these structures, microscopic techniques with none or only limited spectral sensitivity have been employed so far (atomic force microscopy, scanning electron microscopy, transmission electron microscopy). Although these techniques offer a limited potential to distinguish the polymer blocks, a definite and unambiguous attribution of the respective polymer subunits is still lacking.

EXPERIMENTS

We have used the unprecedented opportunities of high brilliance synchrotron radiation at the Advanced Light Source in particular the installed microspectroscopes (PEEM2 at BL 7.3.1.1 and STXM at BL 7.0.1) to investigate the stoichiometric inhomogeneities in those films within the bulk (STXM) and in the surface-near region (PEEM). Our preliminary experiments have explicitly demonstrated the usefulness of these microspectroscopic techniques.

Fig. 1 shows a STXM image of a thin film consisting of a PS-PB-PMMA triblock copolymer (floated on a 100 nm thick Si₃N₄ membrane) recorded at a photon energy of 293 eV (image size: 60 x 60 μm²). The lower image shows a cross section along the red bar clearly indicating the distinct film thicknesses in the sample. This finding is in accordance with the lamellar structure which is formed in bulk of those materials. Brighter spots give a clear indication of an additional lateral fine structure within the homogenous areas. The structures in the upper left corner of Fig. 1 are due to partial dewetting of single terraces.

Fig. 2 shows two XPEEM images recorded at the positive and negative slope of the prominent π^* -resonance ($h\nu = 286.5$ eV) reflecting a distinct contrast reversal which is due to the different termination of the various terraces, i.e. in one case the terrace consists mainly of the PS species whereas in the other areas PMMA is the prominent species. Images recorded at the O K-edge

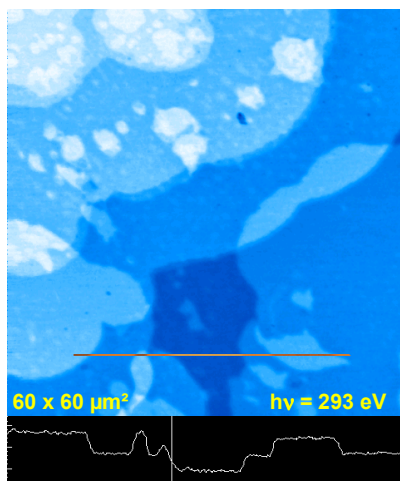


Fig. 1: STXM image of a PS-PB-PMMA-triblock copolymerfilm.

allow much higher magnification due to the higher photon flux and thus allow direct imaging of the lateral patterning, which is dominated by the dewetting of the organic film. The finding of differently terminated areas is fully consistent with previous indirect conclusions drawn from AFM data and thus represents a direct spectroscopic proof.

In both cases, PEEM and STXM, the microdomain formation within a terrace with periodicities on the order of up to several 10 nm can at present not be resolved. XPEEM of soft matter films at present is limited to lateral resolutions of about 100 nm and, in addition, may lead to misinterpretations of the spectroscopic data since the high photon flux densities lead to fast degradation/fragmentation of the organic molecules or even conversion into graphite. STXM partly overcomes the latter restriction since the illumination time is significantly shorter. Much higher transmission (by a factor 100 to 1000 at comparable magnification) of the electron optics in an aberration-corrected XPEEM (like, e.g., at PEEM3 or SMART) will improve spectroscopic imaging of surfaces of soft matter films.

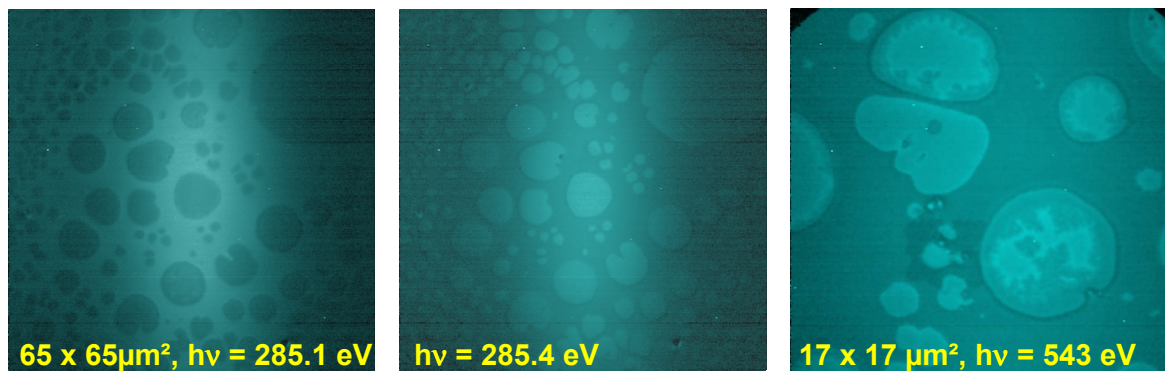


Fig. 2: PEEM images of a PS-PB-PMMA triblock copolymer film indicating the spectroscopic contrast (contrast reversal in the XPEEM images by 0.3 eV photon energy variation). Left and center: excitation at the C K-edge; right: excitation at the O K-edge at higher magnification. Note, that the surface has been plasma-etched to remove the top PB layer.

REFERENCES

- [1] W. Stocker, J. Beckmann, R. Stadler, J.P. Rabe, *Macromolecules* **29**, 7502 (1996).
- [2] H. Elbs, K. Fukunaga, G. Sauer, R. Stadler, R. Magerle, G. Krausch, *Macromolecules* **32**, 1204 (1999).
- [3] K. Fukunaga, H. Elbs, G. Krausch; *Langmuir* **16**, 3474 (2000).
- [4] N. Rehse, A. Knoll, R. Magerle, G. Krausch; *Phys. Rev. Lett.* **87**, 035505 (2001)

This work was supported by the Bundesminister für Bildung und Forschung, contracts 05SL8WW18 and 05KS1WCA1. We gratefully acknowledge experimental support by A. Scholl and A. Doran during the experiments at PEEM2. Many thanks to A.P. Hitchcock for providing the AXIS 2000 program for data evaluation.

Principal investigator: Rainer Fink. Experimentelle Physik II, Universität Würzburg.
Email: raifi@physik.uni-wuerzburg.de Telephone: +49-931-888-5163.